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LETTERS TO THE EDITOR

Complexes of Crown Ethers with 3-Nitro-1,2,4-triazole and Pyrimidine-2,4-dithione

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An indispensable condition for the formation of crystalline host–guest molecular complexes [1, 2] of crown ethers (hosts) with guest molecules is that proton-donor centers be present at one C, N, or O atom (in particular, H_2N, H_2NSO_2, H_2NCS, H_2NH NCO, H_3N^+, $H_2C=$, H_3C, CH_3O, and similar groups or water molecules [1, 2]) to stabilize the components of the complex by hydrogen bonding. The bonding generally involves two protons of the guest donor group, and the stability of the complexes decreases in the order $OH_2 > NH_2 > CH_2$ [3]. Rare examples of crystalline host–guest complexes are known, formed by the most effective [3, 4] 18-membered crown ethers **Ib** [5] and **V** [6–8] with guest molecules whose labile protons are attached to adjacent α-proton-donor atoms (each bearing one proton) intervened by a valence bond (maleic anhydride [5–7] and 2-thiouracil [8]).

The aim of the present work was to find out the possibility of synthesis of molecular complexes of crown ethers of various structure with host molecules bearing by one proton on two α-proton-donor atoms intervened by a valence bond.

It was established that spontaneous evaporation of the solvents from solutions of crown ethers **I**–**V** with heterocycles **VI** and **VII** gives rise to crystalline molecular complexes: **Ia** · **VI** (complex **VIII**), **Ib** · 2**VI** (complex **IX**), **II** · 2**VI** (complex **X**), **V** · 2**VI** (complex **XI**), **Ib** · **VII** (complex **XII**), **II** · **VII** (complex **XIII**), **III** · **VII** (complex **XIV**), **IV** · **VII** (complex **XV**), and **V** · **VII** (complex **XVI**).

Thus, the formation of stable crystalline complexes of neutral organic molecules **VI** and **VII** with crown ethers with macrocyclic cavities of different size (**Ia**, **Ib**), with different aromatic and aliphatic substituents (**II**, **III** and **IV**, **V**, respectively), as well as with differently sterically shielded sides of the macroring (**IV**, **V**) suggests that the binding of crown ethers into host–guest complexes with molecules bearing by one proton on two proton-donor centers intervened by a valence bond is not accidental, and this circumstance should be taken into account in simulation of molecular interactions of natural molecules [1, 9], as well as in purposeful synthesis of host–guest complexes of crown ethers with proton-donor molecules.

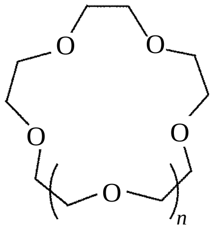
Crystalline molecular complexes VIII–XVI. To 1 mmol of crown ether **I**–**V**, 1 mmol of compound **VI** in acetone–hexane (1 : 1) or 1 mmol of compound **VII** in methanol–ethyl acetate (1 : 2) was added, and the mixture was left to evaporate at 20°C. The monocrystalline precipitate that formed was separated, washed with the same solvent mixture, and dried in air.

Complex of 1,4,7,10,13-pentaoxacyclopentadecane with 3-nitro-1,2,4-triazole, 1 : 1 (VIII), yield 90%, mp 110–112°C. ^1H NMR spectrum, δ, ppm: 3.53 s (20H, CH_2O), 8.86 s (1H, CH). Found, %: C 43.15; H 6.61; N 16.84. $C_{12}H_{22}N_4O_7$. Calculated, %: C 43.11; H 6.63; N 16.76.

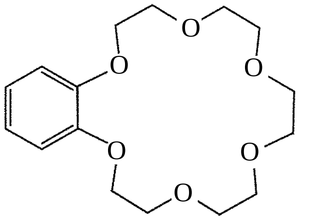
Complex of 1,4,7,10,13,16-hexaoxacyclopentadecane with 3-nitro-1,2,4-triazole, 1 : 2 (IX), yield 88%, mp 184–186°C. ^1H NMR spectrum, δ, ppm: 3.50 s (24H, CH_2O), 8.86 s (2H, CH). Found, %: C 39.11; H 5.76; N 22.84. $C_{16}H_{28}N_8O_{10}$. Calculated, %: C 39.03; H 5.73; N 22.75.

Complex of 2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine with 3-nitro-1,2,4-triazole, 1 : 2 (X), yield 81%, mp 94–96oC. ^1H NMR spectrum, δ, ppm: 3.58 m, 3.72 m, 4.05 m (20H, CH_2O), 6.88 m (4H, Ar–H), 8.86 s (2H, CH). Found, %: C 44.41; H 5.28; N 20.77. $C_{20}H_{28} \cdot N_8O_{10}$. Calculated, %: C 44.45; H 5.22; N 20.73.

Complex of *cis-syn-cis*-eicosahydrodibenzo[*b,k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine with 3-



Ia, Ib



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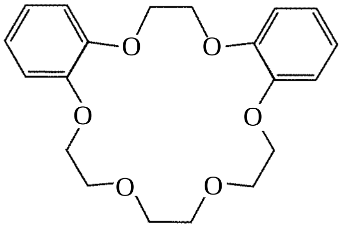

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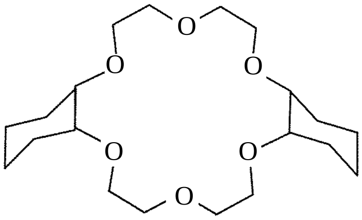

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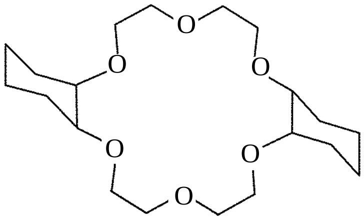
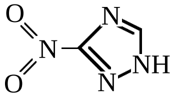
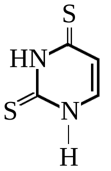


V



VI



VII

I, *n* = 1 (**a**), 2 (**b**).

1,4,7,10,13-pentaoxacyclopentadecane (**Ia**), 1,4,7,10,13,16-hexaoxacyclooctadecane (**Ib**), 2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine (**II**), 6,7,9,10,12,13,20,21-octahydrodibenzo[*b*,*h*][1,4,7,10,13,16]hexaoxacyclooctadecine (**III**), *cis-syn-cis*-eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine (**IV**), *cis-anti-cis*-eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine (**V**), 3-nitro-1,2,4-triazole (**VI**), pyrimidine-2,4-dithione (**VII**).

nitro-1,2,4-triazole, 1:2 (XI), yield 87%, mp 178–180°C. ^{1}H NMR spectrum, δ, ppm: 1.20–1.71 m, 3.52 m (36H, CH_2O, CH_2, CH), 8.86 s (2H, CH). Found, %: C 48.08; H 6.76; N 18.73. $C_{24}H_{40}N_8O_{10}$. Calculated, %: C 47.99; H 6.71; N 18.66.

Complex of 1,4,7,10,13-pentaoxacyclopentadecane with pyrimidine-2,4-dithione, 1:1 (XII), yield 93%, mp 164–166°C. ^{1}H NMR spectrum, δ, ppm: 3.50 s (24H, CH_2O), 6.49 d, 7.24 d.s (2H, CH). Found, %: C 47.13; H 6.89; N 6.97. $C_{16}H_{28}N_2O_6S_2$. Calcualted, %: C 47.04; H 6.91; N 6.86.

Complex of 2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine with pyrimidine-2,4-dithione, 1:1 (XIII), yield 85%, mp >250°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 3.55 m, 3.73 m, 4.05 m (20H, CH_2O), 6.90 m (4H, Ar–H), 6.49 d, 7.25 d (2H, CH). Found, %: C 52.56; H 6.13; N 6.24. $C_{20}H_{28}N_2O_6S_2$. Calculated, %: C 52.61; H 6.18; N 6.14.

Complex of 6,7,9,10,12,13,20,21-octahydrodibenzo[*b*,*h*][1,4,7,10,13,16]hexaoxacyclooctadecine with pyrimidine-2,4-dithione, 1:1 (XIV), yield 80%, mp 236–238°C. ^{1}H NMR spectrum, δ, ppm: 3.59 m, 3.72 m, 4.07 m (16H, CH_2O), 6.96 m (8H, Ar–H), 6.49 d, 7.25 d (2H, CH). Found, %: C 57.08; H 5.63; N 5.58. $C_{24}H_{28}N_2O_6S_2$. Calculated, %: C 57.12; H 5.59; N 6.22.

Complex of *cis-syn-cis*-eicosahydrodibenzo[*b*,*k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine with pyrimidine-2,4-dithione, 1:1 (XV), yield 83%, mp >260°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 1.20–1.71 m, 3.55 m (36H, CH_2O, CH_2, CH), 6.49 d, 7.25 d (2H, CH). Found, %: C 55.82; H 7.84; N 5.45. $C_{24}H_{40}N_2O_6S_2$. Calculated, %: C 55.79; H 7.80; N 5.42.

Complex of *cis-anti-cis*-eicosahydrodibenzo[*b*,*k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine with pyrimidine-2,4-dithione, 1:1 (XVI), yield 91%, mp >250°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 1.23–1.68 m, 3.53 m (36H, CH_2O, CH_2, CH), 6.49 d, 7.25 d, (2H, CH). Found, %: C 55.76; H 7.83; N 5.49. $C_{24}H_{40}N_2O_6S_2$. Calculated, %: C 55.79; H 7.80; 5.42.

The ^{1}H NMR spectra were obtained on a Varian VXR-300 (300 MHz) instrument in DMSO-d_6, internal reference TMS. Crown ethers **IV**, **V** were prepared according to [10], Compounds **I**–**III**, **VI**–**VII** were purchased from Aldrich and used as received.

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REFERENCES

1. *Host Guest Complex Chemistry. Macrocycles: Synthesis, Structures, Applications*, Vögtle, F. and Weber, E., Eds., Berlin: Springer, 1985.
2. *Comprehensive Supramolecular Chemistry*, Lehn, J.-M., Atwood, J.L., Davies, J.E.D., MacNicol, D.D., and Wogtle, F., Eds., Oxford: Pergamon, 1996, vols. 1–11.
3. Elbasyony, A., Brugge, H.J., Deuten, K., Dickek, M., Knochel, A., Kopf, J., Mezer, D., and Rudolp, S., *J. Am. Chem. Soc.*, 1983, vol. 105, no. 22, p. 6568.
4. Ganin, E.G., *Khim. Geterotsikl. Soedin.*, 1997, no. 22, p. 1571.
5. Elbasyony, A., Klimes, J., Knochel, A., Oehler, J., and Rudolp, S., *Z. Naturforsch. B*, 1976, vol. 31, p. 1192.
6. Fonar', M.S., Simonov, Yu.A., Dvorkin, A.A., Ganin, E.V., Kotlyar, S.A., and Malinovskii, T.I., *Dokl. Akad. Nauk SSSR*, 1989, vol. 306, no. 5, p. 1129.
7. Ganin, E.V., Kotlyar, S.A., Musienko, G.S., Fonar', M.S., Salakhov, M.S., Dvorkin, A.A., and Simonov, Yu.A., *Khim. Geterotsikl. Soedin.*, 1989, no. 10, p. 1329.
8. Fonar', M.S., Simonov, Yu.A., Ganin, E.V., Yavolovskii, A.A., and Lyuboradskii, R., *Kristallografiya*, 1989, vol. 44, no. 6, p. 1076.
9. Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, Weinheim: VCH, 1995.
10. Ganin, E.V., Makarov, V.F., Kotlyar, S.A., and Luk''yaenko, *Zh. Obshch. Khim.*, 1988, vol. 58, no. 6, p. 1309.